Pulse Effects at Anodes and Cathodes

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Pulse theory will be used to explain what actually happens in the solution and at the electrode surface of the anode and cathode during a current or voltage pulse. What happens during the time period when the current and voltage are turned off will also be explained. Combining the anodic, cathodic and off-time effects will be used to illustrate what happens during pulse periodic reverse plating.

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When two identical metal electrodes are placed in a solution containing the same metal dissolved as solvated ions, the solution and the electrodes are in both chemical and electrical equilibrium. There is no charge separation. Once a rectifier is turned on and a potential established on the electrodes several things happen. Positively charged ions move towards the cathode. Negatively charged ions move towards the anode, an area of charge separation forms adjacent to the electrodes and current begins to flow through the cell. The rectifier is supplying electrons to the cathode and removing them from the anode. For practical purposes the excess charge or the charge deficit resides on the surface of the electrode. The bulk of the solution is electrically neutral having all the positively charged species offset with an equal amount of negatively charged species. However in the region immediately adjacent to the electrodes there exists an area where charge separation exists. This is called the double layer or inner diffusion layer. As more metal gets plated out the Nernst diffusion layer forms and is between 10 and 200 microns thick. The actual thickness is dependent upon the metal ion concentration, current density, agitation and temperature.

Charge Separation Models

There are 4 models that describe this area of charge separation. They are:

1. Helmoltz model
2. Gouy- Chapman model
3. Stern model
4. Grahme model

The earliest model is that of Helmoltz. He assumed that all excess charge on the electrode is located on the surface of the electrode and that all excess charge in solution is lined up in the same plane. This is similar to a parallel plate capacitor and is shown in figure 1. This shows the solvated metal ions adjacent to the cathode and separated form the cathode by the water molecules in the coordination sphere of the metal ion. This is called the Helmoltz compact model.

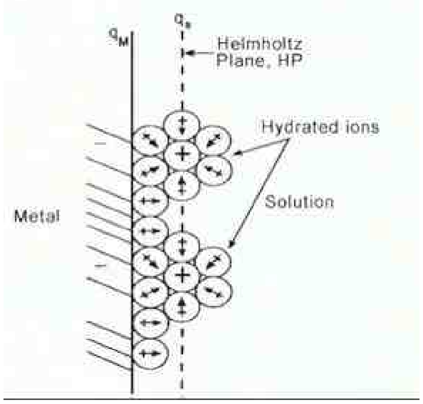

Figure 1, Helmoltz model,
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Gouy and Chapman improved on Helmoltz's model by saying that the solvated metal ions are not all in a plane but are statistically distributed according to an exponential function. The charge separation is less the further away from the electrode. This model is also similar to a parallel plate capacitor but with the plates further apart than the in the Helmoltz model. See figure 2.

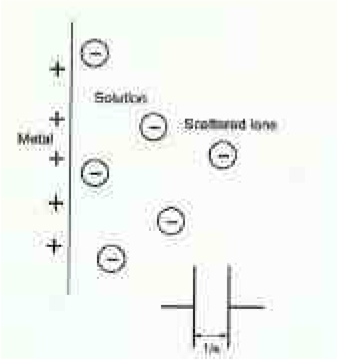

Figure 2, Gouy-Chapman model
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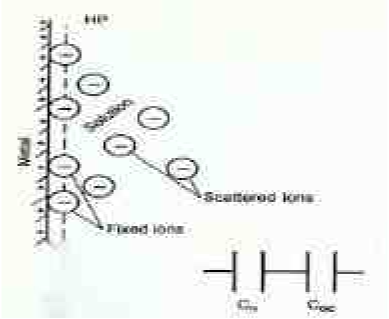

Figure 3, Stern model
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Stern further improved on the model by combining the theories of Helmoltz and Gouy-Chapman. He said that there is the compact inner layer according to Helmoltz and also the diffuse outer layer according to Gouy-Chapman. This model says that there are 2 parallel plate capacitors in series. Stern's model gives excellent correlation to experimental evidence as long as the valence of the ions does not change. See figure 3.

This leads us to the Grahame model. Grahame added another layer and now we have a triple layer model that incorporates anions into the picture. This is shown schematically in figure 4. This model gives excellent correlation with experimental data.

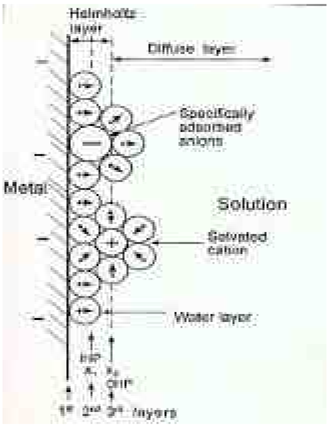

Figure 4, Grahme model
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These models describe what is going on in the double layer but not what is happening at the electrode surface. Lets look at the anode and cathode separately.

Cathode

When a DC rectifier is turned on, the metal ions align themselves into compact and a diffuse layers – called the double layer. Charge is transferred from the cathode to the adjacent solvated metal ions. This can occur in a single step or a multiple process as in the case of copper. The metal ions release the water or anions from their coordination sphere and form neutrally charged metal atoms on the surface of the cathode. These neutral metal atoms are called adatoms. The adatoms are mobile on the cathode surface. The adatoms can then form a new grain. This is

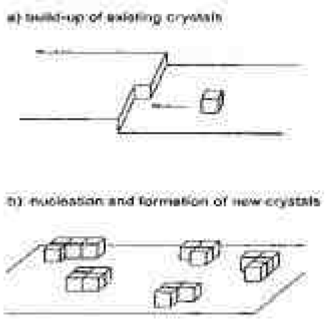

Figure 5, Difference between nucleation crystallization.

called nucleation or they can move into an existing crystal structure and this is called crystallization.

The other main reaction that can occur at the cathode is the reduction of water into hydrogen gas and the hydroxide ions. If the formation of hydroxide is too high it is possible that the hydroxide reacts with the metal ions in the diffusion layer and causes a burnt deposit which is a mixture of metal and metal hydroxides.

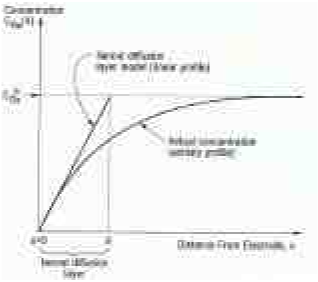

Figure 6, DC diffusion layer

Figure 6 shows how the concentration of solvated metal ions change as a function of distance from the cathode using DC. The concentration of metal ions is less than in the bulk solution for a distance ranging between 10 to 200 microns depending upon the current density, chemistry, temperature and agitation.

Now lets take a look in more detail at what happens during a current pulse. During the time that the pulse is on the same reactions take place as happen with DC, but they are limited by the amount of time the pulse is on.

During the time that the pulse is off several things happen and these are similar to what happens when a DC rectifier is turned off. During the off time:

Hydrogen gas and hydroxide can move away from the cathode
Inner diffusion layer is replenished
additives migrate into the diffusion layer
The plated out metal can recrystallize and grains can grow
Immersion plating can occur

During the off time, hydrogen gas be diffuse away from the cathode, Hydroxide ions move away from the cathode and can react with any buffering agents or hydrogen ions in the solution and solvated metal ions can move towards the cathode to replace those that have been plated out. Also it is possible for plated grains of metal to recrystallize into larger grains. This is most common for gold and copper with off times more than 10 times longer than the on time. In a bath containing 2 dissolved metal ions it is possible for the more noble metal to immersion plate onto the less noble metal.

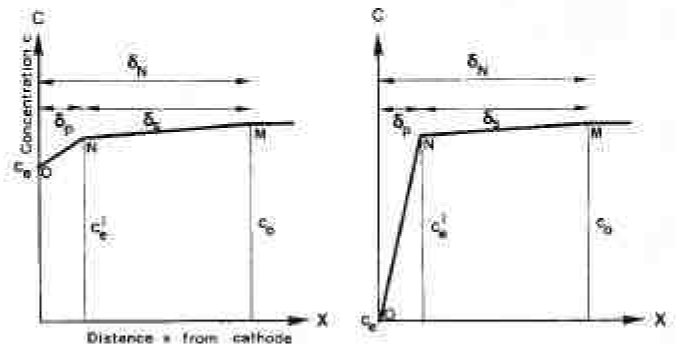

Figure 7 shows what the concentration of metal ions in the diffusion layer at the beginning and at the end of the pulse. Note that it is possible to get the metal ion concentration close to zero at the cathode without any burning of the deposit. At a given current density, the outer diffusion layer is the same distance away from the cathode for both pulse and DC.

Figure 7, Metal concentration in diffusion layer at start and end of pulse

Anode

With DC, at the anode the reactions are similar but in the opposite direction. When the rectifier is turned on the anions align themselves into a compact layer and diffuse layer next to the anode. Metal atoms move out of the crystal structure and become mobile on the surface of the anode. Charge is transferred in either a single step or multiple step process. The soluble metal ions pick up water or anions in their coordination sphere, and then diffuse into the bulk solution.

The other primary reaction that can occur is the oxidization of water, where water is oxidized into oxygen gas and hydrogen ions.

During the on time of a pulse the reactions are similar to what happens with DC. During the off time oxygen and hydrogen ions move away from the anode and /or can react with chemical species in the bath. The solvated metal ions move into the bulk solution and additives can be desorbed from the anode.

Effect of pulse timing

When the rectifier turns on it takes a finite amount of time to charge up the capacitive later. At 20 amps per square foot, the charging time is of the order of 9 milliseconds and the discharge time approx 60 microseconds. So if the rectifier goes from zero to some preset voltage or current in essentially zero time then a fraction of the current is stored in the capacitive layer. When the rectifier is turned off this current is released. By using very short on times which are close to the charging time of the double layer, a good portion of charge is stored in the double layer. When the pulse is turned off, the double layer releases this charge and plating can take place during the off time. See figure 8.

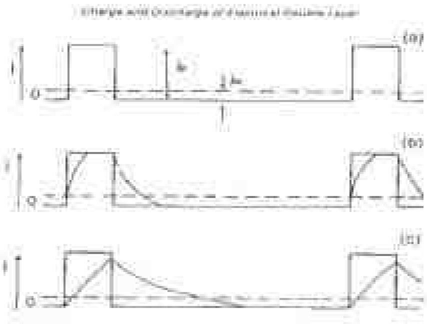

Figure 8, Charge and discharge of double layer for varying pulse widths

With no additives, soluble anodes

A typical PPR cycle is shown in figure 9. During the on time of the pulse metal plates out at the cathode and dissolves from the anode. The fraction of the current going into these reactions is called the anode and cathode current efficiency. The electrodes do not know if they are anodes or cathodes so by rapidly reversing the polarity at the rectifier, the cathode becomes an anode and vice-versa. If different currents and times are used in each direction it is possible to plate at a low current density on the cathode and then rapidly reverse the polarity and deplate for a short high current density cycle. Because the current densities are different in each direction, the low forward current density promotes uniform plating. The high anodic current density deplates more form the edges than from the low CD area. All in accordance with the secondary current density distribution.

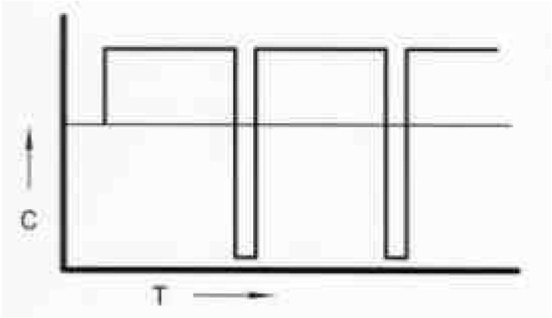

Figure 9, typical PPR cycle

With additives, soluble anodes

Lets talk specifically about copper. An acid copper bath typically contains 2 organic additives. The first is a suppressor to slow down the plating. This is typically a long chain polymer that is not active at the anode or cathode. It functions by being adsorbed on the surface and slowing down the plating rate. The second additive is a small molecule called a brightner or accelerator. It gets consumed or decomposed at the cathode. The brightner is designed so that it displaces the accelerator from the surface and increases the plating rate. Very strange to slow down and increase the plating rate in the same bath. However this does make sense because of the diffusion rate differences between the brightner and suppressor. Looking at a high aspect ration hole or via, the suppressor is adsorbed on the surface and in the hole before the rectifier is turned on. During the cathodic cycle, the brightner displaces the suppressor and accelerates the plating. During the anodic cycle the brightner is desorbed. Being smaller, the brightner diffuses into the hole or via much faster than the suppressor and increases the plating rate in the hole or via but not on the surface where it is easy for the suppressor to diffuse.

Summary

The reactions that take place at the anode and cathode are identical for DC and for pulse. The main difference is that the current is interrupted and during this off time the inner diffusion layer has time to be replenished. By periodically reversing the potential at the electrodes, again the same reactions take place as with DC except the cathode periodically becomes an anode which allows for redistributing the plating thickness with the net effect being better leveling.